

PRINTED COPY. P42510WO leadline

# PATENT SPECIFICATION

Inventor: JOSEPH BERNARD COTTON

**697,294**



Date of filing Complete Specification: Sept. 5, 1951.

Application Date: Sept. 5, 1950. No. 21826/50.

Complete Specification Published: Sept. 16, 1953.

Index at acceptance:—Class 82(ii), F3(a : b).

## COMPLETE SPECIFICATION

### Improvements in or relating to the Colouring of Copper and its Alloys

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the colouring of copper and copper rich alloys and in particular to the formation of an antique green colouration or patina thereon which resembles the natural surface which forms 15 on such metal due to prolonged atmospheric weathering.

It is well known that it is possible to accelerate the formation of patina on copper and its alloys, and many methods of 20 carrying out the operation have been proposed. It has been proposed, for example, to apply a solution of ammonium sulphate and hydrochloric acid to the surface of the metal by a brushing technique, but in this and other methods the 25 results obtained leave much to be desired. For example, it has been difficult to obtain a satisfactory finish free from patchiness, and truly resembling the colour of a 30 naturally formed patina. Moreover, the degree of adhesion has been poor.

The object of the present invention is to provide an improved artificial patina for copper and copper rich alloys wherein the 35 above disadvantages are simply and effectively overcome.

According to the present invention we provide an improved method of obtaining an artificial patina on the surface of 40 copper and copper rich alloys which comprises spraying thereon an aqueous solution containing a double salt of copper and ammonia, but not containing any free acid.

[Price 2/8]

It has been found that the double salt copper ammonium chloride ( $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ ), produces a pure green patina but in order to produce a surface which more closely resembles the natural patina produced on copper due to long term atmospheric weathering, the said double salt is applied with an amount of ammonium sulphate in the form of a solution, the effect being to produce a patina having blue-green colour.

A typical composition of a solution as 55 above described might contain, for example: Copper Ammonium Chloride 20 gms. Ammonium Sulphate 10 gms. Water 100 gms.

It has further been found that uniformity 60 of the artificial patina is best attained, whether ammonium sulphate is present or not, when the solution is allowed to form in droplets over the surface of the metal. This may be achieved by applying the 65 solution through a fine spray nozzle, but preferably the formation of discrete droplets is assisted by the addition to the solution of a small amount of an agent promoting the formation of droplets such 70 for example as commercial trimethyl hexanol, sold under the Registered Trade Mark "Nonanol," or an organic silicon compound, e.g., as sold under the Registered Trade Mark "Antifoam A." By the 75 addition of such substances, the liquid is caused to retract into small globules when applied to the metal surface.

Thus a suitable solution for forming an artificial patina by spraying may have the 80 following composition:—

Copper Ammonium Chloride	20 gms.
Ammonium Sulphate	10 gms.
"Antifoam A"	0.02 gm.
Water	100 gms. 85

After the solution has been applied and

Price 4/- 6/-

has dried out, it has been found that it is essential that the prepared surface shall not be subjected to substantial or prolonged wetting until it has been exposed to weathering processes having certain critical humidities. The effect of premature soaking is to cause the patina to flake or peel.

We have found that to produce a satisfactorily adherent patina, the relative humidity should be between 85% and 100%, although humidities as low as 65% may be used providing that the period of weathering is accordingly lengthened. If the humidity is less than 65%, the patina is likely to peel after subsequent soaking.

The applied coating may however be subjected to a treatment which obviates the necessity for these critical humidity conditions. In this treatment the prepared surfaces are faintly dampened by application of a fine mist or spray of water, in such manner that the dampened surface dries within a short period of time, preferably within five minutes. This procedure may be repeated at intervals of not less than two hours between each dampening until the requisite patina has formed.

It will be appreciated that the patina may be applied to prefabricated elements provided that the humidity or dampening treatments are carried out under controlled conditions. Again should it be required to produce the patina on an existing outdoor surface, the prevailing and forecast weather conditions should be taken into account before commencing treatment. It will be seen however, that the process as applied to erected structures may be assisted by the application of dampening sprays or mist in the manner already described.

What we claim is:—

1. An improved method of forming an artificial patina on the surface of copper and copper base alloys which comprises spraying thereon an aqueous solution containing a double salt of copper and ammonia, but not containing any free acid.

2. A method according to claim 1, in which the solution contains in addition an agent promoting the formation of droplets such for example as commercial trimethyl hexanol.

3. A method according to claim 1 or 2, in which the solution contains in addition ammonium sulphate.

4. A method according to claim 1, 2 or 3, in which the double salt consists of cupric ammonium chloride ( $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ ).

5. A method according to any of the preceding claims, in which the applied coating of solution is subjected to a treatment comprising spraying with a fine mist or spray of water in such manner that the dampened surface dries within a short period of time, preferably within five minutes.

6. A method according to claim 5, in which the treatment is repeated at intervals of not less than two hours until the requisite patina has formed.

7. A method of forming an artificial patina on the surface of copper and copper base alloys substantially as hereinbefore described.

8. Copper and copper base alloy articles provided with an artificial patina by a method in accordance with any of the preceding claims.

J. W. RIDSDALE,  
Agent for the Applicants.

## PROVISIONAL SPECIFICATION

### Improvements in or relating to the Colouring of Copper and its Alloys

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to the colouring of copper and copper rich alloys and in particular to the formation of an antique green colouration or patina thereon which resembles the natural surface which forms on such metal due to prolonged atmospheric weathering.

It is well known that it is possible to accelerate the formation of patina on copper and its alloys, and many methods of carrying out the operation have been proposed. It has been proposed, for example, to apply a solution of ammonium

sulphate and hydrochloric acid to the surface of the metal by a brushing technique, but in this and other methods the results obtained leave much to be desired. For example, it has been difficult to obtain a satisfactory finish free from patchiness, and truly resembling the colour of a naturally formed patina. Moreover, the degree of adhesion has been poor.

The object of the present invention is to provide an improved artificial patina for copper and copper rich alloys wherein the above disadvantages are simply and effectively overcome.

According to the present invention we provide an improved method of obtaining an artificial patina on the surface of copper and copper rich alloys which comprises

spraying thereon a solution containing a double salt of copper and ammonia, but not containing any free acid.

It has been found that the double salt 5 copper ammonium chloride ( $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ ), produces a pure green patina, but in order to produce a surface which more closely resembles the natural patina produced on copper due to long term 10 atmospheric weathering, the said double salt is applied with an amount of ammonium sulphate in the form of a solution, the effect being to produce a patina having blue-green colour.

15 A typical composition of a solution as above described might contain, for example:

Copper Ammonium Chloride	20 gms.
Ammonium Sulphate	10 gms.
Water	100 gms.

20 It has further been found that uniformity of the artificial patina is best attained when the solution is allowed to form in droplets over the surface of the metal. This may be achieved by applying the solution through 25 a fine spray nozzle, but preferably the formation of discrete droplets is assisted by the addition to the solution of a small amount of substance such as commercial trimethylhexanol, sold under the Registered 30 Trade Mark "Nonanol," or an organic silicon compound e.g., as sold under the Registered Trade Mark "Antifoam A." By the addition of such substances, the liquid is caused to retract into small 35 globules when applied to the metal surface.

Thus a suitable solution for forming an artificial patina by spraying may have the following compositions:—

Copper Ammonium Chloride	20 gms.
Ammonium Sulphate	10 gms.
"Antifoam A"	0.02 gm.
Water	100 gms.

After the solution has been applied and

has dried out, it has been found that it is essential that the prepared surface shall 45 not be subjected to substantial or prolonged wetting until it has been exposed to weathering processes having certain critical humidities. The effect of premature soaking is to cause the patina to flake or peel. 50

We have found that to produce a satisfactorily adherent patina, the relative humidity should be between 85% and 100% although humidities as low as 65% may be used providing that the period of 55 weathering is accordingly lengthened. If the humidity is less than 65% the patina is likely to peel after subsequent soaking.

The applied coating may however be subjected to a treatment which obviates 60 the necessity for these critical humidity conditions. In this treatment the prepared surfaces are faintly dampened by application of a fine mist or spray of water, in such manner that the dampened surface 65 dries within a short period of time, preferably within five minutes. This procedure may be continued at intervals of not less than two hours between each dampening until the requisite patina has formed. 70

It will be appreciated that the patina may be applied to prefabricated elements provided that the humidity or dampening treatments are carried out under controlled conditions. Again should it be required to 75 produce the patina on an existing outdoor surface, the prevailing and forecast weather conditions should be taken into account before commencing treatment. It will be seen however, that the process as applied 80 to erected structures may be assisted by the application of dampening sprays or mist in the manner already described.

J. W. RIDSDALE,  
Solicitor for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1953.  
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.

**THIS PAGE BLANK (USPTO)**